DYNAMICS OF WETTING IN BRAZING AND SOLDERING

Technical Report WAL TR 650/1

by

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Associate Professor of Metallurgy
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Contract No. DA-19-020-505-ORD-4917
Boston Ordnance District
OCO, R and D Branch Project No. TB4-003
Department of the Army Project No. 5B93-32-003
Army Materials Research Agency
Watertown Arsenal
Watertown 72, Massachusetts

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ABSTRACT

The spreading by wetting of some liquid metals on substantially clean solid surfaces is a two speed process with the rate of spreading related to contact angle, oxygen traces, and solid state surface alloying.

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I. INTRODUCTION

The object of this work was to study the dynamic behavior of liquid metals spreading on solid metal surfaces, and to determine the influence of environmental factors on wetting.

The experiments performed in the course of this work fell into four categories:

1. Measurement of the rate with which metal droplets of known volume spread on a heated, horizontal plate.

2. Observation of liquid transport through a capillary aperture.

3. A study of the influence of environment (oxidizing, reducing, inert) on the rate with which droplets spread on a heated, flat surface.

4. Measurement of the instantaneous dynamic contact angle of a metal droplet spreading over a flat, heated surface.

The systems studied were:

1. Pure tin and tin-copper liquid alloys spreading on phosphorous deoxidized OFHC solid copper.

2. Liquid silver-copper eutectic alloy spreading on solid commercial grade copper.

3. Liquid silver-copper eutectic alloy (with and without lithium) spreading on solid plain carbon steel (SAE 1020).

4. Liquid commercial brazing alloy (45% Ag, 15% Cu, 16% Zn, 24% Cd) spreading on solid plain carbon steel (SAE 1020).

5. Liquid commercial brazing alloy (45% Ag, 15% Cu, 16% Zn, 24% Cd) filling capillary apertures in plain carbon steel (SAE 1020).

6. Liquid silver-copper eutectic alloys filling capillary apertures in plain carbon steel (SAE 1020).

The spreading or wetting experiments were conducted in both a vacuum furnace and an inert atmosphere furnace constructed for this project. The capillary flow studies were conducted only in the inert atmosphere furnace. Visual and cinematographic methods were used to measure the behavior of the systems studied.

During the course of the investigation it developed that chemical effects completely dominate the dynamics of wetting and spreading, that under certain conditions any of the alloys studied will spread at extremely high velocities, and similarly, any of the alloys studied could be completely inhibited from spreading, even under conditions of truly clean metallic contact. As it turned out, tin and tin-rich alloys provided the only medium within which systematic variations in wetting velocity could be observed. All silver-based brazing alloys wet either very slowly or very rapidly; it was quite impossible to develop environmental conditions which gave intermediate rates, and rapid wetting took place at such very high velocities that it was only

possible to make order of magnitude measurements. For this reason, in the interest of developing fundamental general information on factors which influence wetting rate, tin alloys were selected as a medium for most of the quantitative studies, in spite of the fact they are not regarded as commercial brazing alloys and were not specifically mentioned in the contract scope of work.

All of the studies were conducted under conditions as clean as or cleaner, with respect to environment and surface preparation, than those ever encountered in commercial brazing. There was no attempt to study the effects of interfering impurity films on wetting, although this sort of pursuit might well provide information of real value in future work, and might eventually provide some basis for distinguishing among different brazing alloys. Under clean contact conditions, the different silver-base brazing alloys appear to exhibit closely similar spreading characteristics.

A. Vacuum Furnace

A vacuum chamber and heating furnace were constructed for this study. An overall view of the apparatus is shown in Figure 1. The apparatus provided for separate heating of the solid surface and melting of the brazing alloy, bringing the two to a common temperature before contact. Provisions for the necessary manipulations and also for cinematography were constructed into the top of the vacuum chamber.

The furnace used in the vacuum chamber consisted of coiled elements wound through a grooved, high density, molded ceramic form much in the same manner as a hot plate. Several resistance elements were evaluated and the nichrome element was found to be most suitable for the purposes of this investigation. The heating element was then placed on a supporting platform constructed from four stainless steel rods. Several layers of pure nickel radiation shields were placed in series around the edges, bottom and part of the top of the furnace. A heavy copper temperature equalizing plate supported the experimental plate positioned in the center. The furnace and shielding are visible inside the vacuum chamber in Figure 1.

An automatic controller, operating from two thermocouples, brazed to grooves in the temperature equalizing plate, could be pre-set to $\pm$ 5° C., and held maximum fluctuations to less than $\pm$ 1° C., the maximum accuracy with which calibrated thermocouples could be read using a swinging-light galvanometer.

B. Inert Atmosphere Furnace

An inert atmosphere furnace was constructed for experiments dealing with alloys containing volatile Cd, Zn, and Li.

A graphite cylinder 6 inches in diameter and 12 inches high served as an inert atmosphere chamber. The top lip of the graphite cylinder was filed smooth and level, and covered with a vycor port. The samples to be studied were placed inside the chamber, on the bottom which was externally heated. The temperature of each experiment was measured and controlled by embedding a thermocouple tip into the sample plate.

III. EXPERIMENTAL PROCEDURE

A. Vacuum Furnace

Prior to each experiment, solid copper plates were prepared for exposure to the brazing alloy. Both phosphorus deoxidized and oxygen free high conductivity copper were used. Preparation included cutting, polishing, cleaning, and in some cases etching the surface with an oxidizing acid. The purpose of etching some of the sample surfaces was to compare the spreading behavior with that on "reduced", or oxygen free surfaces. The latter samples were prepared by careful cleaning, and, in some cases, by surrounding the sample plate with graphite during a run.

The alloys to be melted and deposited on the copper plates were prepared by induction melting and included the following compositions of tin and copper in addition to Ag-28% Cu:

Pure Sn

Sn - 2.41% Cu

Sn - 3.89% Cu

Sn - 5.25% Cu

The as-melted alloys were in the form of cylindrical pins 1/8 inch in diameter. Samples were cut from each pin as required, then accurately weighed.

The actual method of placing the spreading alloys on the copper plate was as follows: First, the furnace was brought up to the desired temperature. After the base plate and spreading sample was

prepared, the base plate was placed on top of the temperature equalizing surface. The spreading sample was then mounted with a wire clip to the end of a lever arm attached to the end of a position control rod. The control rod entered the chamber through the copper top by means of a rotary, push-pull vacuum seal. After the furnace reached the predetermined temperature for each experiment, the control rod was rotated and lowered such that the sample was positioned slightly above the hot base plate. Thermal equilibrium was established in less than 15 seconds, because the drops were of small mass, and the liquid drop was then brought into contact with the base plate. The motion picture camera was running while the drop made contact and spread, and continued to operate until motion of the spreading drop either ceased or covered the entire specimen plate. Wetting rates were measured directly from the films.

The capillary experiments, carried out in the inert atmosphere furnace, were performed using annular steel disks placed above a steel base plate by means of steel shims. The steel base plate 3" x 1/16" was centered in the bottom of the chamber. Three steel shims, 0.003" thick, were placed 120° apart. The disks were centered over the shims, then the entire assembly was tack welded. A sample of the brazing alloy to be studied was placed near the hole in the disk, and the system was closed, purged with inert gas, and heated. When the melting temperature of the brazing sample was reached, contact was established, and the latter flowed into the aperture between the shimmed-up disk and base plate. The flow time was measured visually and photographically.

Two methods were used for measuring contact angles: (1) Metallographic observation of sectioned droplets in which spreading was interrupted by gas quench, and (2) light reflection during spreading. The second is depicted schematically in Figure 2, and is used to determine the instant at which the contact angle, which continually decreases during spreading, attains a certain predetermined value. With the motion picture camera in its position vertically above the drop, a light is positioned so that the path from the light to the drop makes an angle, 2θ, with the vertical. Early in the wetting process, while the drop is still quite convex, and the contact angle is greater than θ, the light will be reflected into the camera from that location on the drop whose tangent plane makes an angle θ with the horizontal flat surface. As the drop flattens, the point of reflection moves radially outward, finally reaching the perimeter of the drop, and then disappears. At the instant the light is being reflected from the very perimeter and is about to disappear, the contact angle is θ. By using several lights at different positions, the contact angle can be determined as a function of time.

The method shows much promise in that it can be rendered very precise and fast. As practiced in this investigation, contact angles smaller than 5° could not be observed by light reflection, because this was the smallest angular displacement between camera and light source which could be accommodated. This limitation put the fast-spreading

situations out of range, and it was quickly established that the slow-spreading combinations could be accurately observed by gas quenching and metallography.

With respect to techniques, ultra high speed cinematography, coupled with the necessary optics for observing light reflection at angles less than 1^{o}, could be developed for precise observation of very rapid low angle wetting, which has, in this investigation, been found characteristic of silver-base brazing alloys. It is felt this would prove a fruitful area for further study which would lead to improved fundamental understanding of wetting phenomena in brazing.

IV. RESULTS

A. Rates of Wetting

(1) Spreading of Liquid Drops.

Kinetic data on the spreading of tin and tin alloy drops are summarized in Tables I, II, III, and IV, and in Figures 3, 4, and 5. Many of the observations were made using cinematography from a position directly above the spreading drop, and three views of a spreading tin alloy drop are shown in Figures 3, 4, and 5, at successively longer times after deposition of the drop on the plate. In this way spreading velocity and times could be determined with precision. In Table I are presented data for several runs involving pure tin as the liquid medium, in terms of droplet diameter as a function of time. From these data were prepared Figures 6 and 7. The experimental conditions for each of these runs are set forth in Table II, and the data are presented in different form, giving spreading velocities rather than spreading times, in Table III.

After it had been established that oxygen in trace amounts on the surface to be wetted was vital to the wetting process, various concentrations of an oxidizing acid (HNO_3) were used to prepare the polished copper surface. In no case would any of these be described as heavily oxidized; indeed, after the nitric acid treatment, all of the copper plates upon which wetting

experiments would be conducted had the appearance of clean metallic surfaces. The oxidizing quality of nitric acid depends upon its concentration so that more strongly oxidized surfaces would be expected from higher concentrations. As can be seen in both Figures 6 and 7, those specimen surfaces which were treated with 30 Normal nitric acid were characterized by rapid wetting at velocities well in excess of 1 in/sec. On surfaces etched with dilute nitric acid spreading was quite slow.

Some tests were performed in which, prior to contacting the solid surface with the liquid metal, the solid surface was brought into close proximity to a graphite surface, the whole system being held at high temperature and high vacuum for a long period of time. The objective was to develop a copper surface which was completely free of oxygen. Under high vacuum conditions and at temperatures above 600°C the dissociation of copper oxide in the presence of carbon is rapid and complete. Referring to Figure 7, it is, however, apparent that the times and temperatures involved were insufficient to accomplish any profound change in the wetting character of the copper surface. Those surfaces which had been etched with 30 Normal nitric acid still wet much more rapidly than surfaces which were just polished, or etched with dilute nitric acid and given the graphite treatment.

However, more careful comparison of the wetting behavior of plates etched with concentrated acid indicate the graphite treatment has reduced the rate of wetting. Presumably longer treatment with graphite may have inhibited spreading completely. The two curves labelled 30N + Graphite in Figure 8 relfect two runs made under identical conditions, and convey some impression of the scatter to be expected from data of this kind.

Oxygen has the same effect on silver-base brazing alloys as on tin, as observed in tests with Ag-Cu, Ag-Cu-Cd-Zn, and Ag-Li. With the silver alloys, however, there are no shades of gray. In the complete absence of oxygen, wetting velocities are very low, and in the presence of oxygen, wetting velocities are in excess of 100 inches per second. One important difference between tin and silver-base alloys is that, with the former, it is essential the trace oxygen be initially present on the copper or steel surface. (The wetting behavior of all the tin and silver alloys studied in this investigation was the same on low carbon steel as on OFHC copper.) With the silver alloys the trace oxygen can come from any source including solution in the brazing alloys, the brazing atmosphere, or the solid surface being wetted. In fact, wetting by silver base alloys on copper or steel can be completely inhibited if (a) the brazing alloy is subjected to a preliminary de-oxidation treatment by melting in carbon completely out of contact with the air, and (b) careful precleaning of the solid surface. As with the tin alloys, all of the systems studied would be described as very clean, and certainly free of visible oxides. Even so, trace amounts of oxygen are indeed essential to wetting. With the silver-copper alloys, etching the copper surface with concentrated HNO_3 induced rapid wetting even when de-oxidized alloy was used at high vacuum, when both

the brazing alloy and the solid surface of the copper were as free of oxygen as possible, in atmosphere brazing, very small traces of oxygen in the brazing atmosphere would promote rapid wetting (in fact rather extreme atmosphere control measures were needed to inhibit wetting); finally, in high vacuum brazing on a surface as free as possible of oxygen, rapid wetting obtained in all cases where the brazing alloy was not first subjected to the carbon de-oxidation treatment.

It must be admitted these oxygen effects may be primarily of academic interest, as far as silver brazing is concerned, because it would appear that any practical brazing system would provide enough oxygen to meet the wetting requirements observed in this investigation. In fact, as is widely appreciated, the more practical problem is too much rather than too little oxygen. Based on this investigation it would appear that oxygen only inhibits wetting when enough is present to generate barrier oxide films which interfere with metal-to-metal contact. It remains to be determined how much oxygen a given system can tolerate. The fact that oxygen is not categorically "bad" for brazing, as is widely believed, is an important finding. Oxygen may be an important alloying element for some brazing compositions. Also, passivation or anodizing treatments, such as etching with concentrated nitric, may, in some practical brazing systems, perform the dual function of inhibiting excessive oxidation and providing the

optimum level of surface oxygen. The role of oxygen is a new and important area for research on brazing.

(2) Capillary Flow.

Several experiments were made in which the brazing alloy was permitted to flow through a capillary aperture. It was not possible to make direct observations of wetting velocity, although a rough measurement of the time required to fill the capillary was attempted. The principal finding of this phase of study was that spreading velocities are generally much higher than capillary flow velocities, and capillary flow is completely inhibited when conditions are such that free spreading is slow. It was not found possible to accomplish capillary flow of liquid tin-copper except when the base plate was treated with strong nitric acid.

Although it has been difficult to document experimentally, because capillary flow and spreading velocities with silver-base alloys are so very rapid, some of the motion picture results indicate the alloy spreads over the surfaces of the intended joint before the bulk liquid actually fills the joint. These observations are consistent when viewed in the light of the observed spreading velocities and calculated estimates of the fluid flow resistance offered by the capillary aperture.

B. Metallurgy of Wetting

In Figures 8 through 15 are presented photomicrographs of sectioned droplets in which the spreading was interrupted by inert gas quench.

In Figures 8, 9, and 10 the effects of increasing copper concentration in tin-rich liquid alloy can be easily observed. With a low copper alloy, a thin layer of α solid solution of tin in copper precedes wetting. This forces the conclusion that solid state surface diffusion is an important part of the wetting mechanism for these alloys, because the spreading experiments were conducted at temperatures well below 800°C, which is the lowest temperature α bronze can coexist with liquid; thus development of the α surface layer has to be a solid state reaction. The formation of this α layer removes tin from the droplet and increases its copper concentration. For this reason, the perimeter of the droplet experiences an increase in melting point where isothermal solidification actually inhibits wetting. This is evident from Figure 10, which shows substantially non-wetted contact between 5.25 per cent copper alloy and a pure copper substrate. An intermediate case is shown in Figure 9 which is of 3.89 per cent copper alloy spreading on copper. Figure 9 is characterized by a relatively thick layer of α solid solution beneath and surrounding the droplet.

After a sufficiently long time, the high copper alloy will re-adjust its composition and exhibit delayed spreading. In Figure 11 is shown the 5.25 per cent copper alloy which has been in contact with the copper surface a longer period of time than was the case in Figure 10 and exhibits delayed spreading.

The liquid-solid interface reactions in brazing may be quite complicated. The interface region between pure tin and pure copper is shown at high magnification in Figure 12. In traversing from pure copper to the nearly pure tin (from bottom to top in the Figure), there can be observed a fairly distinct layer of α solid solution which, of course, is continuous with the pure copper substrate, on top of which is a thin complicated mixture of copper-tin intermetallic compounds and, going still further, a rather heavy layer of Cu_3Sn. This layer of Cu_3Sn is characterized by protruding dendrites which reach up into the tin rich droplet. The droplet itself, after being in contact with the copper for some time, has dissolved some copper and, upon solidification, is composed of a more or less uniform dispersion of primary Cu_6Sn_5 in a eutectic mixture of this compound with pure tin.

The wetting and spreading of silver-copper alloy on copper is much less complicated metallurgically because there are no intermetallic compounds. In Figure 13 is shown the type of contact observed between silver-copper alloy and copper under conditions of limited oxygen supply and relatively slow wetting. Figure 14 shows the interface between the

brazing alloy and the substrate copper at high magnification; surprisingly, there is marked porosity present at this interface, the explanation for which is not clear. This porosity was only observed when wetting transpired under high vacuum conditions, which suggests some type of gas evolution was involved. In the complete absence of oxygen, silver-copper alloy assumes a rather large contact angle with copper which is instantly realized when the two are brought into contact, and which changes very slowly with time. In Figure 15 is shown the interface condition associated with long contact of silver-copper eutectic alloy under non-spreading (i.e. ultra low oxygen) conditions. Although the alloy has not exhibited any of the wetting properties commonly associated with it as far as spreading is concerned, there has been "wetting" or penetration of the grain boundaries in the copper. This is more a solution than a wetting effect, which depends on the fact that the liquid was well above the eutectic temperature during contact, and therefore has a high solubility for solid copper.

The most important metallurgical effect uncovered by this investigation was that of oxygen. It is known that oxygen reduces solid-vapor and liquid-vapor surface energies, and there is some reason to suppose that oxygen would also reduce the liquid-solid interfacial energy; the last two effects would promote wetting.

The mechanism by which the liquid-solid interface energy might be reduced would involve oxygen functioning as a covalent bond between the brazing alloy and the solid substrate. This has been observed, for example, to be significant in the wetting or non-wetting contact of liquid iron and graphite. Trace concentrations of either sulfur or oxygen in liquid iron bring about complete wetting of graphite whereas the complete absence of these elements is associated with complete non-wetting. However, this covalent oxygen bond is considered important only for mutual wetting of dissimilar materials. Although there are no data, there is every reason to suppose that the liquid-solid interface energy in combinations like liquid silver on solid copper are so very low that any further reduction by elements such as oxygen would be unimportant. In these systems it is considered the important effect of oxygen is to reduce liquid-vapor surface energy. With systems like liquid silver on solid iron, either or both mechanisms might be important.

C. Contact Angle

With all the tin or silver-base alloys studied as part of this investigation, contact angles during partial or complete wetting were always either greater than 20° or less than 5°. Contact angles greater than 20° were associated with virtually zero rate of spreading. Low but

measureable rates of spreading were observed with contact angles generally the order of 1 - 3 ° (Table IV). With fast spreading it was found quite impossible to "stop" the action and get a quantitative measure of the dynamic contact angle, but it has been established these were always much less than 1°.

The relationships among surface tension and gravity which dictate the shape of a droplet under static partial wetting conditions have long constituted an essential part of surface tension measuring techniques. When the droplet is of sufficiently large volume and shallow depth, approaching the configuration of a bounded film, the shape relations are much simpler and are shown schematically in Figure 16; these relationships depend on the way in which pressure drop across a curved boundary surface depends on the principal radii of curvature, R_1 and R_2. If the film is large enough to have a substantially flat top surface, the pressure within the film will be a simple function of depth, and the shape of the edge of the film is easily calculated. In fact, R_2 is usually so much larger than R_1 that its reciprocal can be ignored, which leads to the statement that the smaller radius of curvature prevailing at the point of contact between the edge of the film and the solid is inversely proportional to the thickness of the film. Thus as a droplet spreads, it becomes more shallow, the radius of curvature at contact becomes progressively larger, and the edge of the film assumes a nearly perfect wedge shape. These statements are only valid for low

rates of spreading where fluid dynamic effects on the shape of the leading edge would be negligible. This provides some basis for estimating the extent to which a liquid film can thin itself by spreading, this extent increasing with decreasing contact angle. With small drops, the analysis is made simpler by the fact that gravity effects become negligible, the pressure in the liquid is essentially uniform, and the surface is therefore spherical. If the maximum altitude of the drop is h and the diameter of the liquid-solid interface is d, the radius of curvature, R, is given by:

$$R = \frac{d^2}{8h} \tag{1}$$

The contact angle, θ, is given by:

$$\sin \theta = 4 \frac{h}{d} \tag{2}$$

For small contact angles, θ, in degrees, is:

$$\theta = 230 \frac{h}{d} \tag{3}$$

Equation (3) is valid for contact angles less than 15°. All of the droplet specimens which spread slowly enough to be gas quenched, were also small enough that gravity effects were negligible, and thus conformed to Equations (1), (2), and, for small contact angles, (3).

At very low rates of spreading, the measurement of contact angles become complicated by penetration. As can be seen in Figures 8 through 10 and also in Figure 14, the liquid-solid interface assumes

an angle to the original solid surface, and this has the effect of reducing the apparent contact angle which one would observe between the exterior of the drop and the unbonded surface of the plate. However as soon as spreading rates become high enough to be of interest in brazing, the penetration influence on contact angle is quite negligible. In fact, closer scrutiny of Figures 8, 9, and 10 clearly shows two stages of wetting, the first slow and the second more rapid. Penetration has had an effect on the initial contact angle, then, as spreading rate increases, the original plate surface at the perimeter of the drop is left intact.

Under certain conditions the contact angle can decrease and cause de-wetting. This has been observed with silver copper eutectic spreading on solid copper under conditions in which the supply of oxygen is very limited. In these occasional cases, spreading would initially be quite rapid, and, shortly after spreading, the film would spheroidize. Tentative explanation for this behavior with silver-base brazing alloys is that the oxygen supply has in some way been exhausted by the wetting reaction, although the detailed mechanism by which this comes about is still a mystery.

D. Fluid Flow

The way in which liquid films migrate over solid surfaces under

the action of external force fields (such as gravity) is fairly well understood, and can be described by the equations presented in Figure 17, which relate the velocity distribution and total velocity of flow to the angle of inclination of the top surface and depth of the film. This mechanism is based, as are most fluid flow relations, on the presumption of zero velocity at the liquid solid interface, and if the external force field is solely responsible for film movement, the type of velocity distribution shown in Figure 17 would require a completely non-wetting contact angle at the leading edge. The spreading of a brazing alloy bears very little relationship to this type of film flow, primarily in that the contact angle in brazing is always very small. The maintenance of a small contact angle in a rapid spreading liquid film requires an unusual velocity distribution which might look something like the lower part of Figure 17, and which would be characterized by maximum velocity in the middle rather than at the top surface of the spreading film. Qualitatively this is known to be the case because motion picture observation of spreading films has shown that the spreading velocity is much greater than the velocity of occasional impurity specks floating on the top surface of the film. The most remarkable thing about rapid spreading at low contact angle is that unbelievably high shear forces would be required at the leading edge of the film if the classical fluid flow mechanism of zero velocity prevails at the liquid-solid interface. It remains to be determined by what mechanism liquids can spread

so very rapidly and still maintain low contact angles.

A few tests performed with plates inclined from the horizontal indicate spreading takes place independent of gravity effects.

Fluid friction is definitely of importance in capillary flow for most brazing systems. An equation for the time required for a brazing alloy to fill a horizontal joint has been given by Udin, et.al.*:

$$t = \frac{3 u l^2}{\gamma d} \qquad (4)$$

where

t = time required for the metal to flow distance, l, in a space of width, d, between parallel surfaces.

u = viscosity of liquid metal.

γ = liquid-vapor surface tension.

Using reasonable values for surface energy and liquid viscosity, calculations show quite clearly that the spreading velocities measured in this investigation are frequently much greater than the maximum flow velocity that could obtain in the capillary filling of a brazed joint. The indications are that spreading and wetting precede and outrun the bulk flow into a brazed joint.

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* Udin, Funk, and Wulff, Welding for Engineers, Wiley, N.Y., 1952.

V. CONCLUSIONS

(1) Spreading by wetting of some liquid metals on substantially clean solid surfaces is a two-speed process, fast, slow, or slow followed by fast. Although these are relative terms, there were orders of magnitude differences in rates between fast and slow spreading, and intermediate rates were not observed.

(2) Fast spreading is associated with contact angles less than 1°, slow spreading with contact angles less than 5°, and all other contact angles were greater than 20°, when the spreading rate was near zero.

(3) Spreading is likely to be faster than capillary flow in brazing systems, and the wetting process leads the filling of the joint by a substantial margin.

(4) Very small traces of oxygen are essential to rapid wetting and spreading. Liquid silver and tin-base alloys will not spread on solid copper or steel in the complete absence of oxygen.

(5) Solid state surface alloying may precede and control the rate of low speed spreading, but do not appear to be of importance in the high speed wetting characteristic of brazing.

TABLE I

Spreading Times of Drops on Flat Surfaces

Time of Spreading (sec)	Diameter of Drop (in.)								
	Exper. 31	Exper. 32	Exper. 34	Exper. 35	Exper. 36	Exper. 37	Exper. 39	Exper. 40	Exper. 41
0.0156	0.331	0.126	0.194	0.179	0.233				
0.0312	0.484					0.241	0.355		0.292
0.0468	0.664								
0.0624	0.677						0.535	0.700	0.334
0.0780	0.785		0.212	0.182	0.272				
0.0936	0.836					0.260			
0.1248	0.950							0.832	
0.1560	0.995	0.169	0.224	0.184		0.260			0.335
0.1872	1.180						0.615		
0.2184						0.297			
0.234				0.218					
0.2496								1.000	
0.312		0.169	0.236	0.269	0.296	0.316	0.664		0.337
0.390				0.284					
0.468		0.185		0.284		0.316		1.130	
0.546				0.287					
0.624		0.190	0.254	0.299		0.334	0.957		0.337
0.780		0.190		0.320	0.296			1.190	
0.936		0.195	0.266	0.329		0.353	1.082		0.348
1.092				0.338					
1.248			0.268	0.344		0.361	1.150		
1.560				0.347	0.333	0.371	1.140	1.200	0.360
1.872		0.198	0.270			0.381			
2.340				0.362	0.342				
2.496			0.274			0.395			
3.120			0.276	0.364	0.346	0.401	1.130	1.250	0.380
3.276		0.198							
3.744		0.198				0.401			
3.900					0.358				
4.680			0.298	0.364	0.358	0.428	1.130		
5.148		0.214							
5.928		0.230							
6.240			0.302	0.364	0.363	0.434	1.130	1.340	0.396
7.800			0.306		0.389	0.440			
9.360							1.140	1.340	0.416
10.92						0.445			

TABLE II

Experimental Conditions for Trials Listed in Table I

Experiment No.	Chamber Pressure (MM. Mercury)	Baseplate Temperature °C	Baseplate* Condition	Spreading* Drop Weight (Grams)	Camera Shutter Speed (Frames/sec.)
30	0.0003	815	Strongly Oxidized.	0.1811	64
32	0.0006	815	Very Mildly Oxidized.	0.0928	64
34	0.0004	816	Moderately Oxidized.	0.1269	64
35	0.0004	816	Moderately Oxidized.	0.1624	64
36	0.0008	821	Very Mildly Oxidized. then Surrounded. with Graphite Shield.	0.1759	64
37	0.0004	818	Polished.	0.1833	32
39	0.0002	845	Strongly Oxidized. then Surrounded. with Graphite Shield.	0.1874	32
40	0.0005	820	Strongly Oxidized. then Surrounded. with Graphite Shield.	0.1984	32
41	0.0003	819	Very Mildly Oxidized. then Surrounded. with Graphite Shield.	0.2275	32

* The baseplate material for all experiments was oxygen free high conductivity copper, and the spreading drop material pure tin.

TABLE III

Velocity Measurements of Spreading Drops as a Function of Time

Time Elapsed after initial contact (sec)	Spreading Velocity (ins./sec.)								
	Exper. 30	Exper. 32	Exper. 34	Exper. 35	Exper. 36	Exper. 37	Exper. 39	Exper. 40	Exper. 41
0.0156	------	0.36	0.31	0.074	0.86	------	-----	------	-----
0.0312	10.75	----	----	-----	----	0.56	10.00	------	1.78
0.0468	6.20	----	----	-----	----	----	-----	------	-----
0.0624	------	----	----	-----	----	----	2.95	3.69	0.50
0.0780	4.51	----	0.23	0.074	0.38	-----	-----	------	-----
0.0936	3.90	----	----	-----	-----	0.12	-----	------	-----
0.1248	3.39	----	----	-----	-----	-----	-----	1.64	-----
0.1560	3.00	0.16	0.12	0.074	-----	0.29	-----	------	0.01
0.1872	2.24	----	----	-----	-----	-----	0.45	------	-----
0.2180	----	----	----	-----	-----	0.40	-----	------	-----
0.2340	----	-----	----	0.87	-----	-----	-----	------	-----
0.2496	----	-----	----	-----	-----	-----	-----	0.01	-----
0.3120	----	0.05	0.12	0.48	0.03	0.13	0.58	------	0.01
0.3900	----	-----	----	0.21	-----	-----	-----	------	-----
0.4680	----	0.03	----	0.06	-----	0.05	-----	0.45	-----
0.5460	----	-----	----	0.06	-----	-----	-----	------	-----
0.6240	----	0.03	0.02	0.06	-----	0.05	0.75	------	-----
0.7800	----	0.03	0.02	0.06	0.03	-----	-----	0.07	-----
0.9360	----	----	0.02	0.06	-----	0.05	0.31	------	0.01
1.2480	----	----	0.02	----	-----	-----	0.05	------	-----
1.5600	----	----	----	----	0.03	-----	0.00	0.02	-----
1.8720	----	----	0.02	----	-----	-----	-----	------	-----

Table IV

Spreading of Alloys on OFHC Copper
(Spreading Interrupted by Gas Quench)

Liquid	Solid Surface	Temperature °C	Thickness to Diameter Ratio After Spreading X 1000	Spreading Time Minutes	Contact Angle
100% Sn	O- Free	315	1.75	35	0.5°
100% Sn	"	560	13.3	16	3.0°
Sn-2.41% Cu	"	660	13.7	3	3.0°
Sn-3.89% Cu	"	660	6.38	2	1.5°
Sn-5.25% Cu	"	660	6.06	4	1.5°
Sn-5.25% Cu	"	660	96.80	2	23.0°
Ag-28% Cu	Etched	900	< 0.1	~ 0	0°
Ag-28% Cu	O-Free	900	10.6	8	2.5°

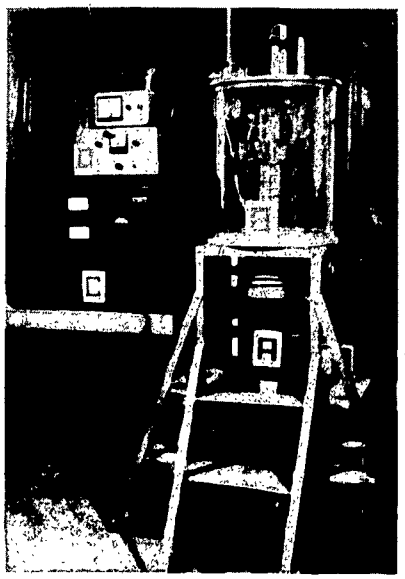
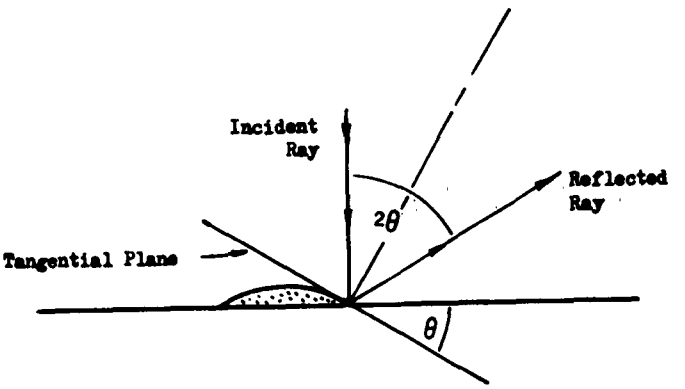


Figure 1

General View of Apparatus



Measurement of Contact Angle by Reflected Light Rays

Figure 2

Geometry of Reflection Scheme for Measuring Dynamic Contact Angles

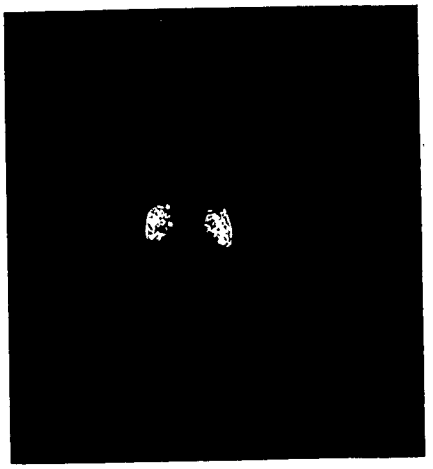


Figure 3

Plan View of Spreading Tin Drop on Copper: 30 Seconds

Figure 4

Plan View of Spreading Tin Drop on Copper: 1 Minute

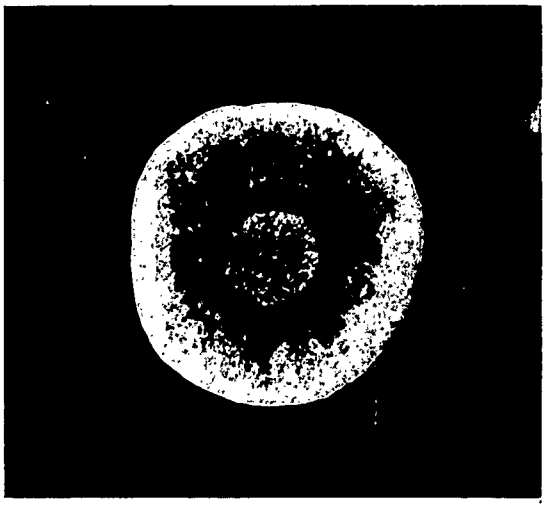


Figure 5

Plan View of Spreading Tin Drop on Copper: 4 Minutes

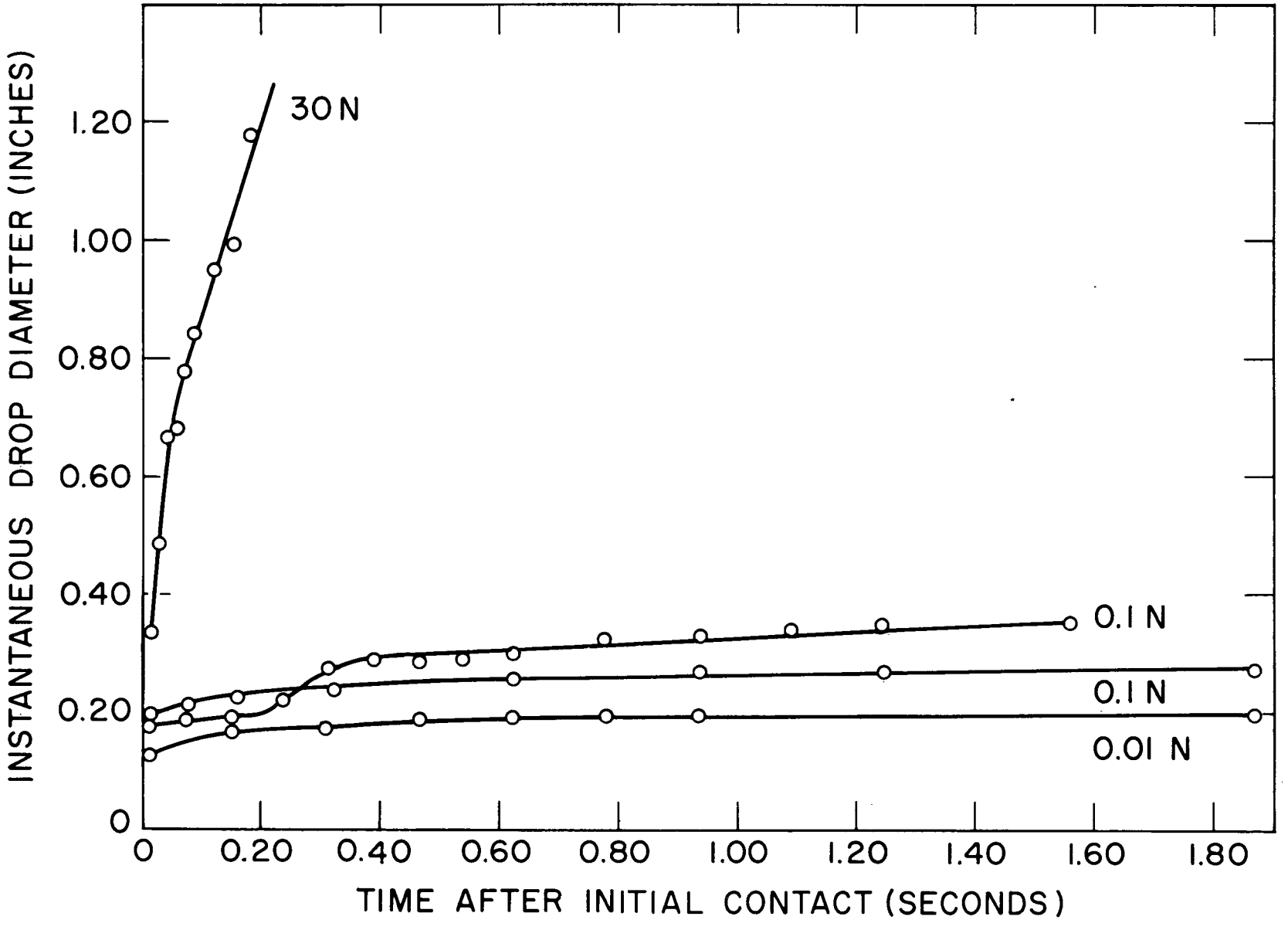


FIGURE 6 SPREADING OF TIN ON COPPER

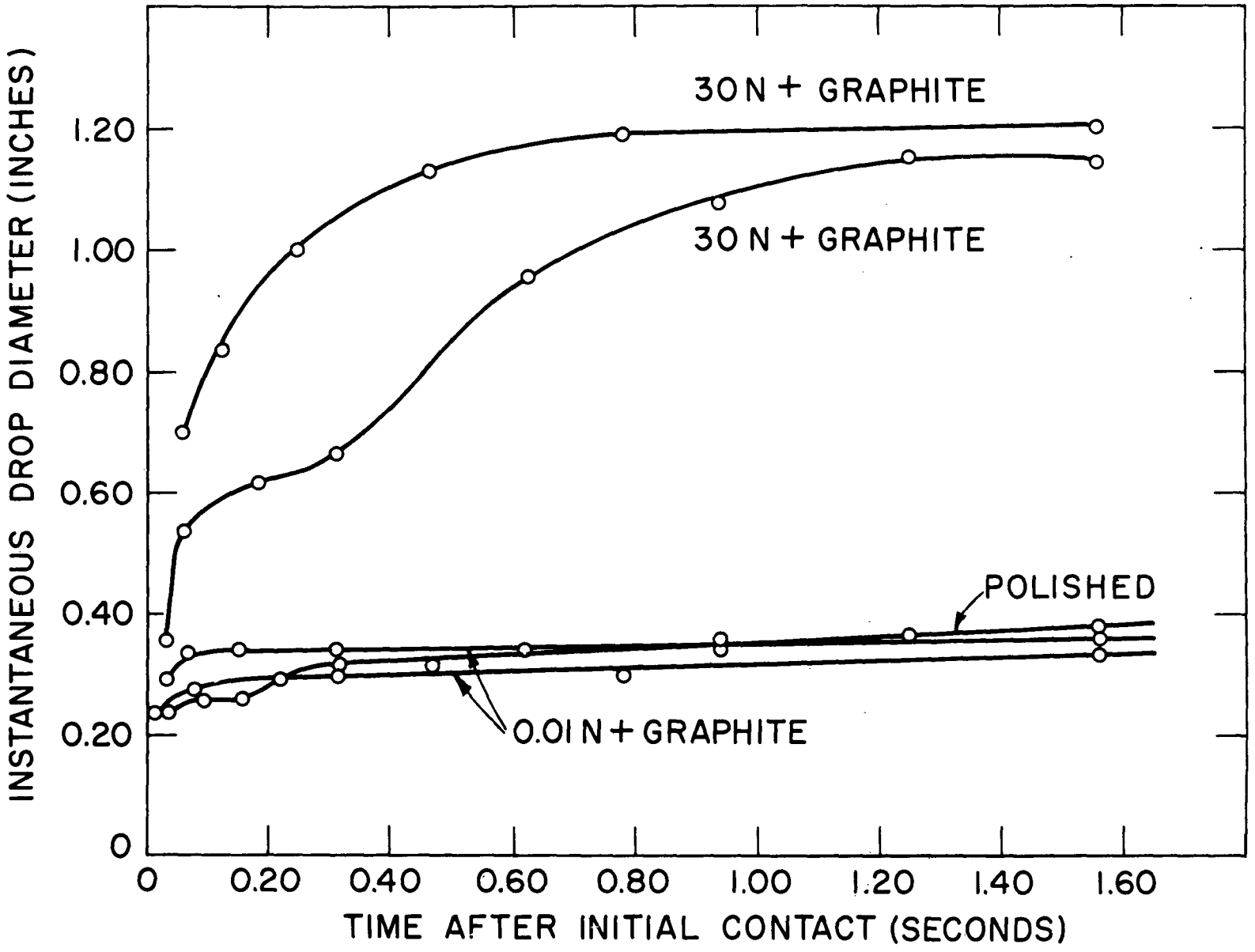


FIGURE 7 SPREADING OF TIN ON COPPER

Figure 8

Edge View (20X) of Interrupted
Spreading of Sn-2.41 % Cu on Copper, 3 Minutes

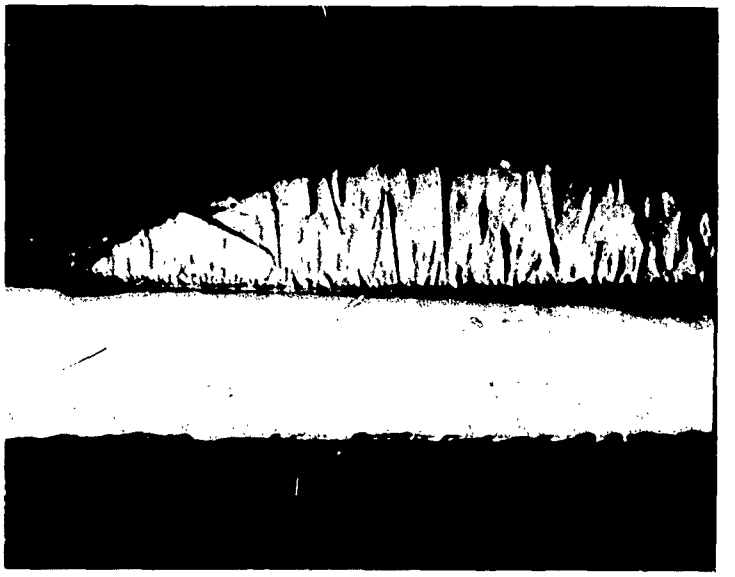


Figure 9

Edge View (20X) of Interrupted
Spreading of Sn-3.89 % Cu on Copper, 2 Minutes

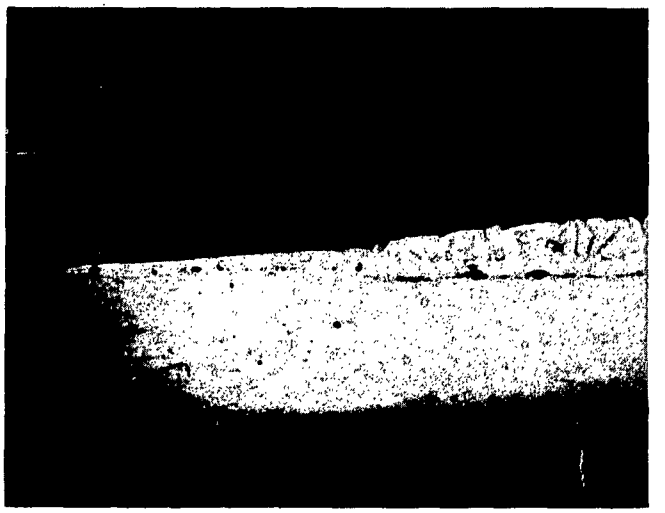


Figure 10

Edge View (20X) of Interrupted
Spreading of Sn-5.25% Cu on Copper, 2 Minutes

Figure 11

Edge View (20X) of Interrupted
Spreading of Sn-5.25% Cu on Copper, 4 Minutes

Figure 12

High Magnification (200X) View
of Interface, Pure Sn Spreading on Copper

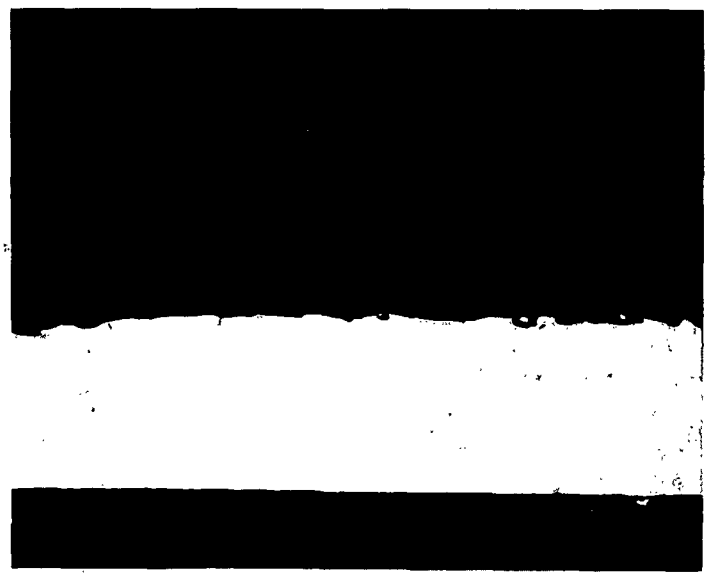


Figure 13

Edge View (20X) of Interrupted
Spreading of Ag-28% Cu on Copper, 8 Minutes (Low-Oxygen)

Figure 14

High Magnification (200X) View of
Interface in Figure 12

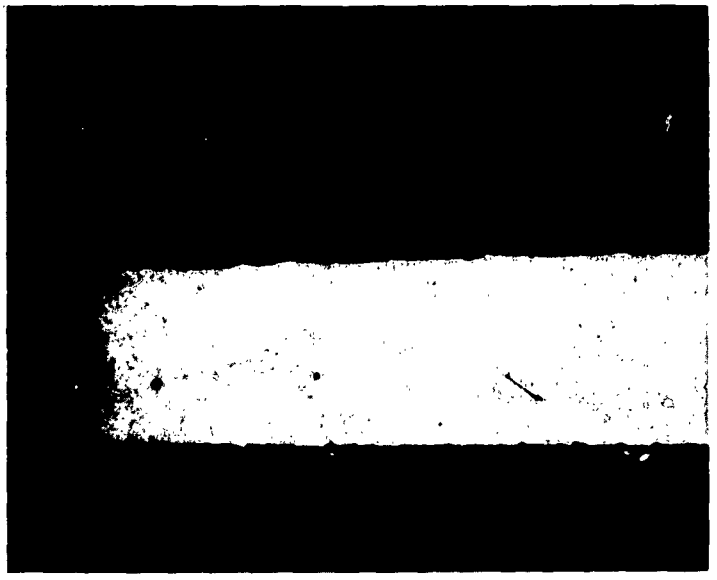


Figure 15

Edge View (20X) of Ag-28% Cu Drop on Oxygen Free Copper
Surface: Penetration but no Wetting

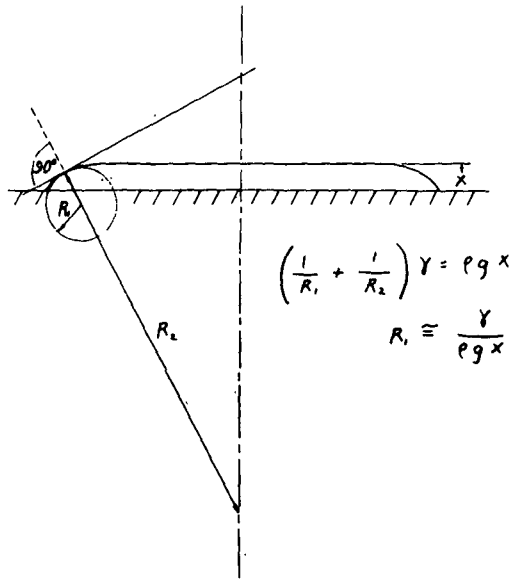


Figure 16

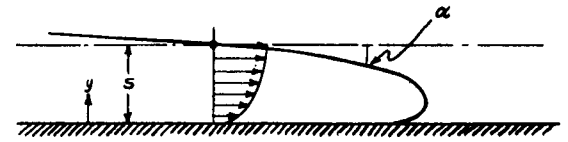
Surface Shape of High Volume Drop at Equilibrium Flat Horizontal Surface

R_1, R_2 = Principal Radii of Curvature

γ = Liquid-Vapor Surface Tension

ρ = Density of Liquid

g = Acceleration Due to Gravity



$$V = \frac{\rho g y \sin\alpha}{2\mu}(2s - y)$$

$$\bar{V} = \frac{\rho g s^2 \alpha}{3\mu}$$

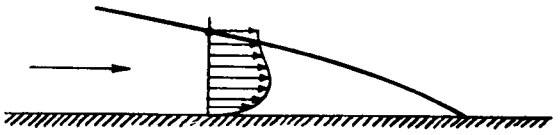


Figure 17

Fluid Flow in Liquid Films

V = local velocity in film

$\bar{V}$ = average film velocity other terms as in Figure 16

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I. In Table I the second column should be labelled Experiment 30 rather than Experiment 31.

II. The caption on Figure 14 should be changed to read "High Magnification (200X) View of Interface in Figure 13" rather than Figure 12.